

# PATENT SPECIFICATION

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## (54) FLUIDITY IMPROVERS

(71) We, MOBIL OIL CORPORATION, a corporation organised under the laws of the State of New York, United States of America, of 150 East 42nd Street, New York, New York 10017, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to improved liquid hydrocarbon compositions and, in one of its aspects, relates more particularly to liquid hydrocarbon compositions having improved fluidity characteristics. Still more particularly, in this aspect, the invention relates to liquid hydrocarbon compositions containing certain olefinic polymeric materials which are effective in improving the low temperature flow properties and pour point characteristics, in such liquid hydrocarbon compositions as crude oils and petroleum residual oils.

Prior to the present invention, various materials have been suggested by the prior art as fluidity improvers in liquid hydrocarbons. In this respect, it has been found that such fluidity improvers have not proved entirely satisfactory with regard to improving the fluidity characteristics of liquid hydrocarbons where the hydrocarbons to be treated boil over a wide range. Furthermore, some fluidity improvers have proved effective in certain types of oils, while exhibiting more limited improvement in other types. More specifically the ability to employ a fluidity improver in liquid hydrocarbons which boil, for example, within the range from 75°F. to 1000°F. and which are also effective in various types of oils, for example, crude oils or petroleum residual oils, is most desirable.

It has now been found, as more fully hereinafter described, that liquid hydrocarbon compositions can be provided possessing improved fluidity characteristics, by incorporating therein relatively small amounts of

certain olefinic polymeric materials. These polymeric materials are esters of 1-olefin maleic anhydride copolymers in which the olefins have at least 22, and preferably at least 30 carbon atoms per molecule. In accordance with the invention, these polymeric materials can be effectively employed in the liquid hydrocarbon compositions as low temperature flow property and pour point improvers in an amount from .001 per cent to 5 per cent, and preferably from 0.01 to 0.5 per cent, by weight, of the total weight of the liquid hydrocarbon compositions. Particularly desirable ester copolymers are those selected from the group consisting of behenyl, Alfol 20T and Alfol 2022T esters of 1-olefin maleic anhydride copolymers, in which, as previously indicated, the olefin has at least 22, and preferably at least 30, carbon atoms per molecule, as more particularly hereinafter described. "Alfol" is a registered Trade Mark.

The liquid hydrocarbons improved in accordance with the present invention may comprise any hydrocarbons in which fluidity improvement is desirable. A field of specific applicability, in accordance with the present invention, is in the improvement of liquid hydrocarbons boiling at a temperature from 75°F. to 1000°F. Of particular importance is the treatment of petroleum distillate oils which have pour and flow points above about 75°F. and which boil as high as about 750°F. or higher. It should be noted, in this respect, that the term "distillate oils" is not intended to be restricted to straight-run distillate fractions. The distillate oils can be straight-run distillate, catalytically or thermally cracked (including hydrocracked distillate oils) or mixtures of straight-run distillate oils, naphthas and the like, with cracked distillate stocks. Moreover, such oils can be treated in accordance with well known commercial methods, such as acid or caustic treatment, hydrogenation, solvent refining, clay treatment, and the like.

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The distillate oils are characterized by their relatively low viscosity, pour point and the like. The principal property which characterizes these hydrocarbons, however, is their distillation range. As hereinbefore indicated, this range will preferably lie between 75°F. and 1000°F. Obviously, the distillation range of each individual oil will cover a narrower boiling range falling, nevertheless, within the above mentioned limits. Likewise, each oil will boil substantially and continuously throughout its distillation range.

As hereinbefore indicated, the liquid hydrocarbon compositions improved in fluidity characteristics through the use of the ester copolymers of the present invention have broad applicability to liquid hydrocarbon compositions in the form of crude oils or petroleum residual oils. Thus, the fluidity characteristics of very high wax-containing petroleum residual oils, such as the residuum of North African crude oils designated as Zelten, or similar petroleum oils which boil above approximately 650°F. and have pour points above 75°F. have broad applicability. Another specific type of crude oil to which the present invention also has broad applicability is the Amal crudes.

As previously described, the novel fluidity improvers of the present invention comprise esters of 1-olefin maleic anhydride copolymers, in which the olefins have at least 22 carbon atoms per molecule. The preparation of these fluidity improvers, is, in general, carried out by copolymerizing one mole of the 1-olefin with one mole of maleic anhydride, at a temperature from about 75°C. to about 175°C., preferably in the presence of an organic peroxide catalyst, for example, di-*t*-butyl peroxide or benzoyl peroxide, or other suitable polymerization catalyst, in an amount sufficient to permit polymerization or copolymerization to take place. Small amounts of the catalyst are usually sufficient for such purposes, for example, amounts from 1 per cent to 10 per cent, by weight, of the polymerization mixture. The 1-olefin maleic anhydride copolymer thus produced is reacted with an alcohol in a mole ratio of from 1:1 to 1:2 to produce the corresponding ester copolymer.

The following data and examples will serve to illustrate the preparation of the novel polymeric materials of the present invention and their efficacy in improving the fluidity characteristics of liquid hydrocarbon compositions. It will be understood, however, that it is not intended the invention be limited to the particular esters of 1-olefin maleic anhydride copolymers, or the particular liquid hydrocarbon compositions described. Various modifications of these compositions, as previously indicated, can be employed and will be readily apparent to those skilled in the art.

The preferred alcohols employed for the preparation of the aforementioned esters of 1-olefin maleic anhydride copolymers are behenyl alcohol, Alfol 20T alcohol, and Alfol 2022T alcohol.

The behenyl alcohol is a commercially available mixture containing, by weight, 0.3% 1-hexadecanol, 15.8% 1-octadecanol, 14.8% 1-eicosanol, 68% 1-docosanol and 0.9% 1-tetracosanol.

The Alfol 20T alcohol is a mixture containing, by weight, 8% 1-octadecanol, 73% 1-eicosanol, 10% 1-docosanol and 2% 1-tetracosanol.

The Alfol 2022T alcohol is a mixture containing, by weight, 2% 1-octadecanol, 63% 1-eicosanol, 25% 1-docosanol and 2% 1-tetracosanol.

#### EXAMPLE 1

A mixture of 49 grams (0.5 mole) of maleic anhydride, 210 grams (0.5 mole) of a mixture of  $C_{30}$  and higher 1-olefins and 7.77 grams (3%) of di-*t*-butyl peroxide was gradually heated to 127°C. with stirring. Heat was shut off at 127°C. The reaction was exothermic, and the temperature rose rapidly to 137°C. and then dropped. After the mixture had been stirred at 150–155°C. for 5 hours, an additional 5.18 grams (2%) of di-*t*-butyl peroxide were added at 80°C. After the mixture had been stirred at 150–155°C. for another 5 hours, another 5.18 grams (2%) of di-*t*-butyl peroxide were added at 80°C. After the mixture had been stirred at 150–155°C. for another hour, the reaction mixture became very viscous and the reaction was immediately discontinued. Altogether, 23.31 grams (9%) of di-*t*-butyl peroxide were added stepwise, and the mixture was stirred at 150–155°C. for 16 hours. The final product, a mixture of  $C_{30}$  and higher 1-olefin-maleic anhydride copolymers, was waxy at room temperature.

#### EXAMPLE 2

A mixture of 64.75 grams (0.125 mole) of a mixture of  $C_{30}$  and higher 1-olefin-maleic anhydride copolymers (Example 1), 82.15 grams (0.25 mole + 3.9 grams excess) of behenyl alcohol, 7.35 grams (5%) of *p*-toluene sulfonic acid and 300 cc of xylene was refluxed at 145°C. until water almost stopped coming over. The reflux temperature was then gradually raised to 175°C. by removing some of the xylene and was held there until water stopped coming over. The reaction product was water-washed, filtered and distilled to 175°C. under house vacuum. The final product, a mixture of the di-behenyl esters of  $C_{30}$  and higher 1-olefin-maleic anhydride copolymers, was waxy at room temperature.

#### EXAMPLE 3

A mixture of 64.75 grams (0.125 mole) of a mixture of  $C_{30}$  and higher 1-olefin-maleic anhydride copolymers (Example 1),

84.15 grams (0.25 mole + 7.65 grams excess) of Alfol 20T alcohol, 7.45 grams (5%) of p-toluene sulfonic acid and 300 cc of xylene was refluxed at 145°C. until water almost stopped coming over. The reflux temperature was then gradually raised to 175°C. by removing some of the xylene and was held there until water stopped coming over. The reaction product was water-washed, filtered and distilled to 175°C. under house vacuum. The final product, a mixture of the di-Alfol 20T esters of  $C_{30}$  and higher 1 - olefin - maleic anhydride copolymers, was waxy at room temperature.

#### EXAMPLE 4

A mixture of 64.75 grams (0.125 mole) of a mixture of  $C_{30}$  and higher 1 - olefin - maleic anhydride copolymers (Example 1), 87.18 grams (0.25 mole + 7.93 grams excess) of Alfol 2022T alcohol, 7.55 grams (5%) of p-toluene sulfonic acid and 300 cc of xylene was refluxed at 145°C. until water almost stopped coming over. The reflux temperature was then gradually raised to 175°C. by removing some of the xylene and was held there until water stopped coming over. The reaction product was water-washed, filtered and distilled to 175°C. under house vacuum. The final product, a mixture of the di-Alfol 2022T esters of  $C_{30}$  and higher 1 - olefin - maleic anhydride copolymers, was waxy at room temperature.

#### EXAMPLE 5

A mixture of 64.75 grams (0.125 mole) of a mixture of  $C_{30}$  and higher 1 - olefin - maleic anhydride copolymers (Example 1), 39.1 grams (0.125 mole) behenyl alcohol, 5.3 grams p-toluene sulfonic acid, and 300 grams xylene was refluxed at 145°C. until water stopped

coming over. The mixture was then stirred at 175°C. for about two hours. The final product obtained by topping at 100 mm pressure at 175°C. was a mixture of the mono-behenyl esters of  $C_{30}$  and higher 1 - olefin - maleic anhydride copolymers.

#### EXAMPLE 6

A mixture of 116.7 grams (0.33 mole) of a  $C_{22-28}$  1 - olefin mixture, 32.7 grams (0.33 mole) maleic anhydride, and 7.5 grams di - t - butyl peroxide was stirred at about 150°C. for about 2 hours to form a mixture of  $C_{22-28}$  1 - olefin - maleic anhydride copolymers.

#### EXAMPLE 7

A mixture of 56 grams (0.125 mole) of a mixture of  $C_{22-28}$  1 - olefin - maleic anhydride copolymers (Example 6), 82 grams (0.25 mole) behenylalcohol, 4.1 grams p-toluene sulfonic acid, and 100 grams toluene was refluxed at 145°C. for about two hours. The mixture was then heated to 185°C. and held at this temperature until the water stopped coming over. The final product was a mixture of di-behenyl esters of  $C_{22-28}$  1 - olefin - maleic anhydride copolymers.

The polymeric materials of Examples 2 to 5 and 7 were subjected to ASTM Pour Test No. D-97 for determination of respective pour points. This test was applied against the undiluted as well as against samples of the same oil containing the indicated concentrations of the polymeric materials produced in accordance with the foregoing Examples. The test oils employed comprised an Amal crude oil and an Amal residual oil having a boiling point of about 650°F. +. The results obtained are shown in the following Table I.

TABLE I  
ASTM Pour Test Results  
(ASTM Test No. D-97)

| Additive         | Amal Crude Oil |                | Amal Residual Oil 650°F.+ |                |
|------------------|----------------|----------------|---------------------------|----------------|
|                  | Concn. Wt. %   | Pour Point °F. | Concn. Wt. %              | Pour Point °F. |
| Uninhibited fuel | 0.00           | 75             | 0.00                      | 95             |
| „ „ + Ex. 2      | 0.06           | 25             | 0.50                      | 75             |
| „ „              | 0.00           | 75             | 0.00                      | 95             |
| „ „ + Ex. 3      | 0.10           | 20             | 0.50                      | 70             |
| „ „              | 0.00           | 75             | 0.00                      | 95             |
| „ „ + Ex. 4      | 0.10           | 20             | 0.50                      | 75             |
| „ „              | 0.00           | 75             |                           |                |
| „ „ + Ex. 5      | 0.10           | 50             |                           |                |
| „ „              | 0.00           | 75             |                           |                |
| „ „ + Ex. 7      | 0.10           | 25             |                           |                |

It will be apparent from the data set forth in the foregoing Table I that the polymeric materials of the present invention are highly effective as fluidity improvers in liquid hydrocarbons. As will be understood, results will vary with respect to the specific polymeric materials employed. In order to accomplish any given improvement, many of the aforementioned polymeric materials can be employed in very small amounts. Others can be effectively employed in the aforementioned practical concentrations from 0.01 to 0.5 percent, by weight, of the liquid hydrocarbon composition.

To further demonstrate the efficacy of the novel polymeric materials of the present invention as fluidity improvers in liquid hydrocarbon, the individual polymeric materials

were next blended into an Amal crude of the type hereinbefore described and subjected to a series of tests for determination of fluidity characteristics by an evaluation of constant shear rates (94 secs.<sup>-1</sup>) at 40°F. The test involves the use of a Ferranti-Shirley viscometer in which the cone is set on a plate sufficiently close to make electrical contact. The cone is rotated at a pre-set speed of 5 r.p.m., and the torque required to maintain this speed is recorded as a function of time. This test was applied against the uninhibited as well as against samples of the same oil containing the indicated concentrations of the respective polymeric materials produced in accordance with the foregoing Examples 2 to 5 and 7. The results obtained are shown in the following Table II.

TABLE II  
Constant Shear Rate (94 sec.<sup>-1</sup>) Test

| Additive             | Concn.<br>Wt. % | Amal Crude Oil                     |  |
|----------------------|-----------------|------------------------------------|--|
|                      |                 | Vis. after 100 sec. Shear<br>Poise |  |
| Uninhibited Fuel Oil | 0.00            | 9.5                                |  |
| " " " + Ex. 2        | 0.06            | 6.9                                |  |
| " " "                | 0.00            | 15.9                               |  |
| " " " + Ex. 3        | 0.06            | 6.33                               |  |
| " " " + Ex. 4        | 0.10            | 6.37                               |  |
| " " "                | 0.00            | 12.2                               |  |
| " " " + Ex. 5        | 0.01            | 4.1                                |  |
| " " "                | 0.00            | 12.2                               |  |
| " " " + Ex. 7        | 0.01            | 8.8                                |  |

From the foregoing Table II, it will be apparent that the polymeric materials of the present invention are also highly effective as fluidity improvers in liquid hydrocarbons on the basis of constant shear rate evaluation.

#### WHAT WE CLAIM IS:—

1. A liquid hydrocarbon composition containing a small amount, sufficient to improve its fluidity characteristics, of an ester of a 1-olefin maleic anhydride copolymer, the olefin having at least 22 carbon atoms per molecule.
2. A composition according to claim 5 in which the olefin has at least 30 carbon atoms per molecule.
3. A composition according to claim 1 or 2 in which the ester is a behenyl or eicosanyl ester.
4. A composition according to claim 1, 2 or 3 in which the polymeric material is present in an amount from 0.001 percent to 5 percent, by weight.

5. A composition according to claim 4 in which the polymeric material is present in an amount from 0.01 percent to 0.5 percent, by weight.

6. A composition according to any of claims 1 to 5 in which the liquid hydrocarbon has a boiling range within the range 75°F. to 1000°F. (25° to 540°C).

7. A composition according to any of claims 1 to 6 in which the liquid hydrocarbon comprises a crude oil.

8. A composition according to any of claims 1 to 6 in which the liquid hydrocarbon comprises a petroleum residual oil.

9. A composition according to any of claims 1 to 8 substantially as herein described with reference to any of Examples 2 to 5 and 7.

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